Protection of palladium catalysts for hydrodechlorination of chlorinated organic compounds in wastewaters

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A B S T R A C T

Palladium is an efficient catalyst for hydrodechlorination (HDC) of aliphatic and aromatic chlorinated organic compounds in water. However, its applicability in water treatment processes is limited because of its sensitivity to catalyst poisons. In the present study, Pd/Al_2O_3 was modified by various silicone-based fillings and coatings. The modified catalysts proved to be active in the HDC of chlorobenzene with $A_{Pd} = 35$–$65 \, L \, g_{Pd}^{-1} \, min^{-1}$ vs. $570 \, L \, g_{Pd}^{-1} \, min^{-1}$ for the unprotected catalyst. It was insusceptible against sulphite as a model catalyst-deactivating ionic water constituent. However, under HDC conditions the silicone appeared to be degraded, becoming gradually permeable for sulphite. Hydrolysis of the silicone polymers, initiated and promoted by the HDC product HCl, is assumed to be responsible for the polymer ageing. Release of chloride from the coated catalyst into the bulk water phase has been revealed as a crucial step in this concept of hydrophobic catalyst protection. It could be shown that with Pd/Al_2O_3, HDC also proceeds in dry organic solvents such as *n*-hexane at significant reaction rates ($A_{Pd} = 18$–$28 \, L \, g_{Pd}^{-1} \, min^{-1}$).

1. Introduction

Chlorinated organic contaminants (COC) are of particular environmental concern due to their high abundance in wastewater and sewage sludge, surface water, groundwater and soils [1–3]. Hydrodechlorination (HDC) using Pd-based catalysts shows a high potential for the destruction of such contaminants in water. HDC is highly efficient and selective in clean water even at ambient conditions [4–6]. However, the noble metal Pd is very sensitive to deactivation in natural waters and wastewaters due to precipitations, dissolved natural organic matter and in particular poisons such as heavy metals and reduced sulphur compounds [4,7–11]. Hydrogen sulphide (H_2S and HS^-) is ubiquitous in natural waters and is one of the strongest Pd poisons. For these reasons, Pd-based catalysts are rarely used for practical applications in water treatment. Only a few field-scale studies have investigated the use of Pd-based catalysts for the HDC of various COC in groundwater [12–14]. The specific Pd activities A_{Pd} of the catalysts applied for various chlorinated aliphatics were as low as 0.1–$0.2 \, L \, g^{-1} \, min^{-1}$, estimated from the data reported by the authors. These values are far below the potential performance of Pd catalysts. The highest specific activity of Pd/magnetite nanocatalysts found under optimized laboratory conditions was reported to be up to 5 orders of magnitude higher [15]. Therefore, in order to exploit the high potential activity of Pd better, it is highly desirable to find ways and means to protect the metal from poisoning.

Several methods have been proposed for increasing the resistance of noble-metal gas-phase catalysts against poisons, including the optimization of the catalyst support [16], the use of permselective coatings [17] and the addition of scavengers to selectively bind the deactivating component [18]. However, these methods still fail to provide a full-scale protection against common catalyst poisons for water treatment by HDC. Countermeasures such as applying alkaline scavengers to bind HCl and thus protect the catalysts from chloride poisoning have been investigated [6]. Schueth et al. placed Pd clusters into hydrophobic zeolites in order to repel ionic catalyst poisons [19]. Fritsch et al. [20] and Kopinke et al. [11] demonstrated successfully the use of hydrophobic polymer coatings as a means of preventing catalyst poisoning for the HDC reaction in water. The polymer coating is permeable for the reactants (i.e. H_2, COC and HCl) and impermeable for ionic or bulky molecules, which could deactivate the catalyst. Poly(dimethylsiloxane) (PDMS) was selected as the polymer coating due to its chemical stability and very high diffusivities for small, uncharged molecules. In these studies, the protection of the catalyst was achieved by the embedding of Pd nanoclusters within thin polymer films, or by coating of Pd/Al_2O_3 particles (63–125 μm). The coated catalysts maintained a relatively high activity after 24 h exposure to soil extracts or to

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the catalyst poison sulphite (50 μM) [11]. However, Fritsch et al. [20] have reported some deactivation of the coated catalyst after several reaction runs, even without the addition of poisons. The authors suggested that this phenomenon could be attributed to partial chloride poisoning. As shown by these studies, the approach of a non-porous hydrophobic polymer coating could be promising for the protection of Pd catalysts against common ionic poisons. However, the long-term stability (i.e. the ability to retain activity over extended time periods) of the coated catalyst still needs to be evaluated.

In the present study, two approaches for protection of Pd/Al$_2$O$_3$ catalyst by PDMS were tested. First, a rubbery PDMS wall-coated batch reactor was designed. This reactor was based on Pd/Al$_2$O$_3$ powder embedded in a PDMS wall coating. Second, several methods for the coating and/or pore-filling of commercially available pelletized Pd/Al$_2$O$_3$ were examined. Usually, the pelletized form of the catalyst is used in established fixed-bed reactors for water treatment [12–14]. Therefore, it is desirable to find ways and means to protect these pellets directly, such that this established reactor type can continue to be operated. For both approaches, the activity and long-term stability of the protected catalysts were evaluated in the absence of poisons. In addition, the ability of the polymer coating to provide a long-term protection against high concentrations of ionic poisons was also tested. It is important to note, however, that this protection method is only efficient for ionic poisons, whereas uncharged molecules such as non-ionic sulphur compounds (H$_2$S, mercaptanes, disulphides, etc.) could still permeate through the polymer. In order to prevent this, an oxidative pre-treatment of the water is advisable [21].

2. Experimental

2.1. Chemicals

The chemicals monochlorobenzene (MCB, >99% purity), trichloroethylene (TCE, >99.5% purity), benzene, methanol, n-hexane, toluene, trimethylchlorosilane (TMCS), sodium bicarbonate (NaHCO$_3$), as well as silicone oil 550, were purchased from Merck, Germany. The two-component PDMS (Wacker SilGel® 612A/B) was purchased from Wacker-Chemie AG, Germany. Sodium sulphite (Na$_2$SO$_3$) was obtained from J.T. Baker. The eggshell catalyst G-133D Pd on γ-Al$_2$O$_3$ was purchased from Commercia, Germany. A crushed and sieved size fraction of the catalyst (d_p = 63–125 μm) as well as the original 3 mm pellets were used for the HDC experiments. Both the crushed fraction and the original pellets contained 0.5% (w/w) Pd, and had a BET surface area of 161 m^2 g^{-1} (N$_2$ adsorption), a porosity of 0.43 cm^3 g^{-1} (N$_2$ adsorption) and a Pd dispersion of 0.16 (CO adsorption).

2.2. Preparation of the coated catalysts

2.2.1. Preparation of a rubbery PDMS wall-coated batch reactor

The two components of the PDMS were mixed together at a ratio of 2:1 (components A, crosslinker and B, platinum catalyst respectively). An amount of 2.86 or 9.53 g (corresponding to a 150 or 500 μm film thickness) of the two-component PDMS blend was mixed with 15 mL hexane. The PDMS–hexane mixture and 50 mg Pd/Al$_2$O$_3$ (d_p = 63–125 μm) were then added to a 250 mL glass reactor vessel. The vessel was placed in a sonication bath (3 min) in order to achieve complete dispersion of the particles. The solvent was then allowed to evaporate overnight, while the cylindrical vessel was gently rotated horizontally (10 rpm). During this period, the cold-curing silicone rubber was formed by cross-linking polymerization. Subsequently, the polymer was dried (40 °C) for 2 d. This procedure resulted in the formation of a homogeneous polymer

film coating at the vessel walls, whereby the catalyst particles were completely embedded within this film. For simplicity, the wall-coated batch reactor will herein be referred to as "batch reactor".

2.2.2. Coating and pore-filling of Pd/Al$_2$O$_3$ pellets

i. *Pore-filling with silicone oil.* An amount of 10 g pellets was added into a 2-neck round-bottom flask and evacuated for 2 h to remove air and water from the pores. About 20 mL of degassed hot silicone oil (70 °C) was then injected into the flask and the mixture was shaken under vacuum for an additional 1 h, after which the excess oil was removed. Due to this impregnation, the pellets gained 25% weight, which corresponds to about 55% pore filling. This procedure was applied to the original commercial pellets and to pellets hydrophobized by pre-treatment with TMCS. For hydrophobization the pellets were treated in a solution of 1% (v/v) TMCS in toluene at 75 °C overnight and afterwards rinsed twice with methanol.

ii. *Pore-filling with silicone oil and external rubbery PDMS coating.* Pore-filled pellets (see i) were coated with an additional layer of the rubbery two-component PDMS. The two liquid PDMS components were first mixed together (2:1, without any solvent), then 15 g of the mixture was added to a flask containing 10 g of pore-filled pellets. After 30 min, the excess liquid PDMS was discarded. The coated pellets were dried (40 °C) for 2 d. The weight gain was 8.7%, which corresponds to an average external film thickness of about 140 μm.

iii. *Double-layer rubbery two-component PDMS coating.* Approximately 10 g of the two-component PDMS mixture was dissolved in 15 mL of n-hexane and added to a flask containing 10 g Pd/Al$_2$O$_3$ pellets. The mixture was purged with N$_2$ for 1 h in order to evaporate some n-hexane, and the pellets were then separated from the solution. Subsequently, the pellets were dried (40 °C) for 2 d. An additional external two-component PDMS coating was implemented as described above in ii.

2.3. Procedures for catalyst testing with HDC reactions

The catalyst testing was performed as batch experiments. Both for the wall-coated reactors and for the 3 mm pellets, the HDC of MCB was conducted in 250 mL glass vessels equipped with a Mininert® valve with 200 mL buffer solution (1 mM NaHCO$_3$ in deionized water; pH 8.7). The solution was first purged with hydrogen gas and then spiked with a stock solution of MCB in methanol ($C_{0,MCB}$ = 10 mg L^{-1}). This marked the start of the HDC reaction (t = 0). During the reaction, the vessel was continuously shaken (120 rpm). The HDC kinetics was monitored by means of headspace sampling (25 μL, gas-tight glass syringe) with GC–MS (Shimadzu GC–MS QP2010) or GC–FID (Shimadzu GC-14B) analysis. At the end of the reaction, the release of chloride to the bulk solution was measured by means of ion chromatography (IC25, Dionex).

In the case of the uncoated pelletized catalyst, a cage-like arrangement of a perforated PTFE tube was used in order to protect the pellets from mechanical damage and dispersion of the particles while avoiding additional mass-transfer resistance. The PDMS coating of the coated pellets provided mechanical protection, no cage was necessary here.

The protection of the PDMS coating against ionic catalyst poisons was tested by adding Na$_2$SO$_3$ (1–120 mM) to the catalyst suspension. For each reaction cycle, the interaction time between the catalyst and the poison was at least 3 d. In alkaline solution, sulphurous acid is mainly deprotonated (pK_{A2} = 7.21), i.e. SO$_3^{2-}$ is the dominating sulphite species.

The stability of the coated catalyst systems against internal HCl formation (i.e. self-poisoning) was tested using TCE at higher concentrations ($C_{0,TCE}$ = 26–37 mg L^{-1}, C_{NaHCO3} = 10 mM).

These experiments aimed at increasing the turn-over number (TON) of the catalyst in terms of internally formed HCl.

A number of reaction cycles were performed with each batch of catalyst in order to test its long-term stability. After each cycle, the solution was replaced by a fresh buffer solution and was then purged with hydrogen gas until all volatile components (desorbing from silicones) were purged-off.

In order to evaluate HDC reaction rates in non-protic organic media (simulating PDMS) and the effect of water on the reaction, batch experiments with the solvent tetrahydrofuran (THF) were performed. The HDC of MCB in THF was monitored, while gradually increasing the amount of water in the reaction medium from 0 to 5.7% (v/v) by spiking with water through the Mininert® valve, during running HDC experiments. Another experiment, with initially 20% water in THF, was conducted separately. In addition, the effect of the native water content of the catalyst on the HDC rate was examined. The native water was removed by consecutive washes of the catalyst with methanol (twice) and THF (once), each for 30 min. Reaction rates for the dried and non-dried catalysts in *n*-hexane were then measured. In all cases, the reaction was performed with an initial MCB concentration of $C_{0,MCB} = 13\,mg\,L^{-1}$ and a catalyst concentration of $C_{catalyst} = 140\,mg\,L^{-1}$ ($d_p = 63$–$125\,\mu m$, $C_{Pd} = 0.7\,mg\,L^{-1}$). The HDC kinetics was monitored by means of GC–MS analysis of liquid samples with toluene as internal standard.

2.4. Data analysis

The HDC reaction of MCB was fitted to a first-order kinetic model by means of linearization on a semi-logarithmic scale. The performance of the catalyst was described by the specific Pd activity (A_{Pd}), defined in Eq. (1) as

$$A_{Pd} = \frac{k_1}{\ln 2 \cdot C_{Pd}} = \frac{1}{\tau_{1/2} \cdot C_{Pd}} \tag{1}$$

where k_1 is the pseudo first-order kinetic rate coefficient, C_{Pd} is the Pd concentration and $\tau_{1/2}$ is the half-life of the substrate. It has been shown that high catalytic activities such as measured in aqueous suspensions of Pd/Al$_2$O$_3$ catalysts are affected by external and internal mass-transfer limitations [22]. Therefore, A_{Pd} and k_1 calculated in the present study have to be considered as apparent rate parameter which describes the overall reaction kinetics inclusive mass-transfer effects.

The stress on the catalyst from the HCl produced during the reaction was evaluated as the TON, which represents the number of HDC events for each surface Pd atom, i.e. the molar amount of HCl produced divided by the molar number of surface Pd atoms.

3. Results

3.1. HDC of the non-coated and coated catalysts in the wall-coated batch reactor

Fig. 1 presents an example for the HDC reaction kinetics of MCB (disappearance) and benzene (formation) for a non-coated catalyst (A), as well as for the coated catalyst in the batch reactor system (B). As can be seen in the figure, the HDC reaction in both cases can be fitted by a first-order kinetic model up to high conversion degrees (≥99%), even though a significant sorption of the organics to the PDMS occurred. The offset of the MCB line in Fig. 1B is due to its rapid sorption to the PDMS film. The sorption capacity for MCB was evaluated by extrapolating its regression line to time $t = 0$. The sorption capacity for benzene was evaluated from the decrease in the final benzene concentration in the batch reactor system compared to the non-coated catalyst system. The degree of sorption of MCB in the 150 μm PDMS batch system was found to
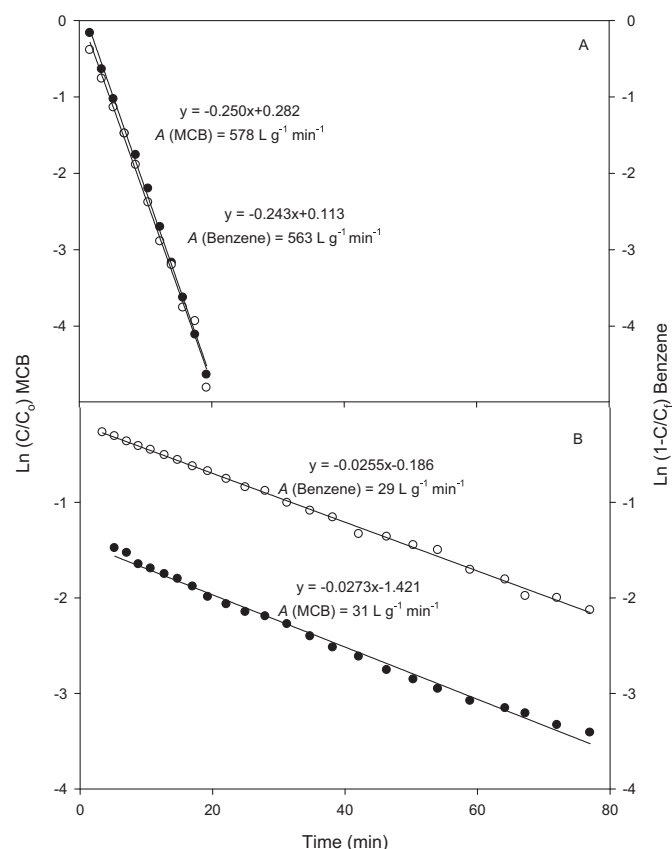

Fig. 1. The HDC reaction kinetics of the non-coated catalyst (A) and of the coated catalyst (B) in the batch reactor system (150 μm thick PDMS). The measurements of MCB and benzene are represented by filled and open symbols, respectively. C_f is the final benzene concentration (corresponding to 100% MCB conversion).

be $(79 \pm 3)\%$, whereas the sorption of benzene was $(55 \pm 1)\%$, corresponding to PDMS–water partition coefficients (K_{PDMS,H_2O}) of 690 and 135, respectively. Koehler [23] found for MCB a PDMS–water partition coefficient of 455 using a different PDMS sample.

Despite the high sorption degrees, the first-order rate coefficients calculated from MCB disappearance and from benzene formation are very similar, and fit well to the expected first-order kinetics [11]. This suggests that partitioning between the phases is much faster than the chemical reaction. Hence, average activity values measured using the MCB disappearance and the benzene formation will be presented from now on.

It was also found that the coating of the 63–125 μm catalyst particles caused a decrease of about 1 order of magnitude in the apparent catalytic activity (A_{Pd}) in a buffer solution free of catalyst poisons (35–65 vs. 570 L g^{-1} min^{-1} for the coated and non-coated catalysts, respectively; see Fig. 2). The decrease in activity depends on the polymer film thickness (150 and 500 μm); a lower activity was obtained for the catalyst embedded in the thicker PDMS film. In comparison, Fritsch et al. [20] and Kopinke et al. [11] found that the apparent activity decreased only by a factor of 2–3 due to the coating with PDMS. However, in these studies the catalyst contained only about 30% (w/w) PDMS [11] or the PDMS film was only a few μm thick [20]. The loss of activity due to the polymer coating can be caused by two groups of effects: (a) additional mass-transfer limitations, caused by (i) lower diffusivities of the reactants in PDMS compared to water, (ii) a higher diffusion path length, and (iii) an additional (and thicker) phase boundary layer at the water–PDMS interface; (b) alternatively, the decrease in activity could be the result of a lower intrinsic Pd activity, due to modifications at the active sites or change of the local reaction medium [11,20,24]. In
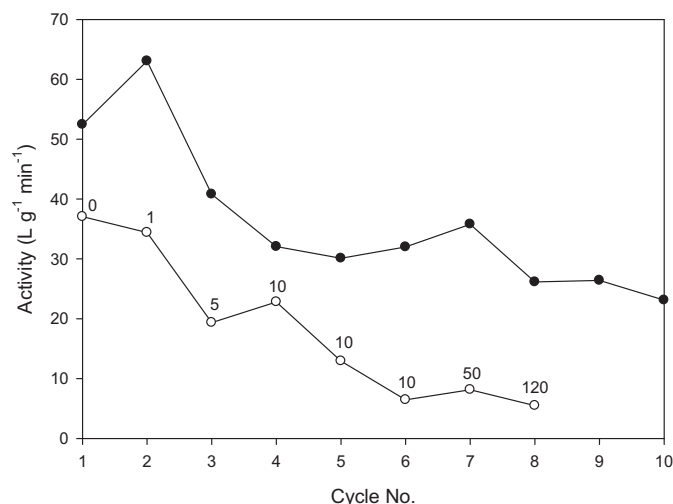
Fig. 2. Specific Pd activities for repeated HDC cycles with $C_{MCB,0}$ = 10 mg L^{-1} in the wall-coated batch reactor (C_{Pd} = 1.25 mg L^{-1}). The bulk solution was either free of catalyst poison (filled symbols, 150 μm thick PDMS) or contained a given concentration of the catalyst poison Na$_2$SO$_3$ (open symbols, 500 μm thick PDMS). The concentrations of poison in each cycle (in mg L^{-1}) are indicated on the graph.

contrast, the activity would possibly tend to be increased by: (c) the sorptive enrichment of reactants close to the active sites, which may be expected to increase reaction rates. However, it is not clear whether local concentrations or thermodynamic activities are rate-determining. The thermodynamic activity of a reactant determines the driving force of its sorption on the catalyst surface. It is lower for the batch reactor system with PDMS films than for the catalyst suspension in pure water (by a factor of 5 for 79% sorption on the 150 μm PDMS film). This could explain the observed decrease in apparent catalytic activities. The effect of the film thickness on the extent of catalyst activity decreases, both in the current study and also in comparison to [20] and [11], is in line with two of the effects mentioned above: it may indicate that (a) mass-transfer limitations such as intrapolymer diffusion play a significant role, or (c) the thermodynamic activity of MCB is decreased when more PDMS is offered as sorption sink. It is important to point out that, despite the decrease in catalyst activity, the initial activities obtained are still 2 orders of magnitude higher than were achieved for practical applications of Pd catalysts in water treatment (≈0.1 L g^{-1} min^{-1}) [12–14].

3.2. Catalyst stability towards ionic poisons and HCl in the wall-coated batch reactor

Fig. 2 shows several HDC reaction cycles with 10 mg L^{-1} MCB in the wall-coated batch reactor, both in the absence and in the presence of the catalyst poison sulphite. The differences in the initial apparent activities of the two reactors are attributed to the different polymer film thicknesses (150 and 500 μm), as explained in Section 3.1. Some deactivation of the catalyst was also observed in the absence of sulphite, so that after 10 reaction cycles (TON ≈ 450) the activity decreased to about 45% of its initial value. Loss of HDC activity with time has been reported for Pd, as well as for Rh, Ni and Pt catalysts [25–27]. It may be speculated that some deactivation is caused by chloride formed in the HDC reaction [16,25], or by a decrease in pH, which would promote Pd leaching [15,28]. Also the formation of carbonaceous deposits is held responsible for deactivation processes [29]. For Pd/Al$_2$O$_3$, it was also proposed that a pH decrease might increase the positive surface charge of the alumina and thus inhibits sorption of electron-rich reactants, such as chlorohydrocarbons, resulting in a decreased HDC rate [28]. However, all

these considerations were made for water rather than for a PDMS phase as local reaction medium. In the current study, the non-coated catalyst (63–125 μm) exhibited a 30% decrease in activity after four HDC cycles under standard conditions (data not shown). This is comparable to the deactivation behaviour of the coated catalyst. In the batch reactor system, the HDC reaction was performed in a buffer solution, so that there was no change in pH of the bulk solution during the experiment. However, the pH in the close proximity of the catalyst particles and inside the pores (i.e. under the PDMS coating) may not have been buffered. Therefore, the observed partial deactivation could be due to both chemisorption of chloride and decrease in the local pH value (traces of water may permeate to the catalyst surface). It is important to note that the decrease in catalyst activities occurred between reaction cycles rather than during each reaction cycle, in which the reaction followed strictly first-order kinetics up to high conversion levels. However, decrease in local pH values or accumulation of chloride would be expected to cause a loss of activity also *during* the HDC reaction, therefore we have to admit that the reasons for deactivation of Pd catalysts are not yet fully understood. It seems that catalyst deactivation is more a long-term than an instantaneous process. In conclusion, in the absence of poisons, the decrease in activity after 10 HDC cycles (total TON of 450) was moderate.

The ability of the polymer coating to provide protection against ionic catalyst poisons was tested by the addition of sulphite at concentrations of 1–120 mM, which correspond to S:Pd$_{surface}$ ratios of 550–65,000 (85–10,000 S:Pd$_{total}$). Although the lowest concentration applied (1 mM) caused a complete deactivation of the unprotected catalyst, the coated catalysts showed much better stability against sulphite. Results for the 500 μm PDMS coating are presented in Fig. 2. The contact time between catalyst and sulphite was 3 d prior to a HDC cycle, and 14 d for the highest concentration applied (120 mM). Altogether, the catalyst was exposed to sulphite solutions for about 45 d. For comparison, the poisoning of non-protected Pd catalysts normally occurs within seconds to minutes [4,19].

From Fig. 2 one can see that the catalyst activity tends to decrease from cycle to cycle irrespective whether sulphite is present or not. It is not clear whether the faster deactivation of the 500 μm catalyst film is due to the impact of sulphite or to thicker PDMS coating. The 150 μm PDMS film proved to be stable against 1 mM sulphite, but did not prevent catalyst deactivation in the presence of 10 mM sulphite (data not shown). Apparently, a certain thickness of the polymer layer is necessary for a long-term protection against high sulphite concentrations.

However, the question has to be raised of how sustainable PDMS coatings are under HDC reaction conditions. It was observed that the sorption characteristics of MCB to the PDMS phase changed with time. For each successive reaction cycle, slower sorption kinetics but higher sorption capacities were obtained (data not shown). This can be deduced from the offsets of the extrapolated MCB regression plots (analogous to Fig. 1) and the time delay until the linear part of the plot starts. These changes in sorption properties reflect changes in the chemical or physical nature of the polymer coating, possibly due to acid-induced hydrolysis processes [30,31].

Chloride measurements showed that the HCl formed during the reaction was not fully recovered in the bulk solution (Fig. 3). Although HCl can be released from PDMS-coated catalysts, a substantial fraction of the chloride formed remains trapped or is consumed. In fact, for the 500 μm film, less than 10% and for the 150 μm film up to about 50% of the HCl formed reach the water bulk phase after five reaction cycles. In theory, undissociated HCl molecules should be able to desorb from the Pd surface and diffuse through the PDMS film, whereas transport of HCl as hydrated ions is expected to be impossible or extremely slow [20]. One can speculate on three possible sinks of chloride: (i) the alumina surface,
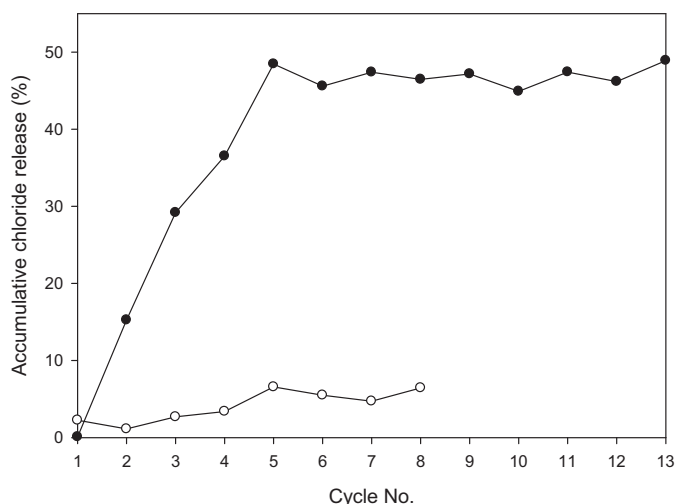
Fig. 3. Release of chloride to the bulk solution in the wall-coated batch reactors. The PDMS film thickness was 150 μm (filled symbols) or 500 μm (open symbols). The HDC reaction was conducted with 10 mg L^{-1} MCB or 29–36 mg L^{-1} TCE.

(ii) the alumina pores, where a concentrated aqueous hydrochloric acid phase may be formed [32] and (iii) the hydrolysis of PDMS, yielding chlorinated organics. The shape of chloride release curves in Fig. 3 indicates that there are several sinks: at least one of them was rapidly saturated, after about 60 μmol of HCl were absorbed in 2.86 g of PDMS plus 50 mg of Pd/Al$_2$O$_3$. Since HCl is known to cause deactivation of Pd catalysts [16,25], the build-up of any chloride pool in the alumina pores would imply that the coated catalyst system could not retain its activity as the TON continues to increase.

Fig. 4 shows the activity of a wall-coated batch reactor over a range of TONs up to 3000. This TON corresponds to 0.8 g of chloride per gram of alumina catalyst. Since no catalyst poisons were added to this reactor until the last cycle, we attribute the loss of activity to chloride accumulation: in effect, a self-poisoning of the catalyst. The activity of the catalyst decreased gradually and then stabilized at about 25% of its initial activity. At this steady state level, about 50% of the chloride formed was released to the water bulk phase.

In order to understand the fate of HCl formed in the batch reactor system, the capacity of the Al$_2$O$_3$ pore-system for aqueous HCl
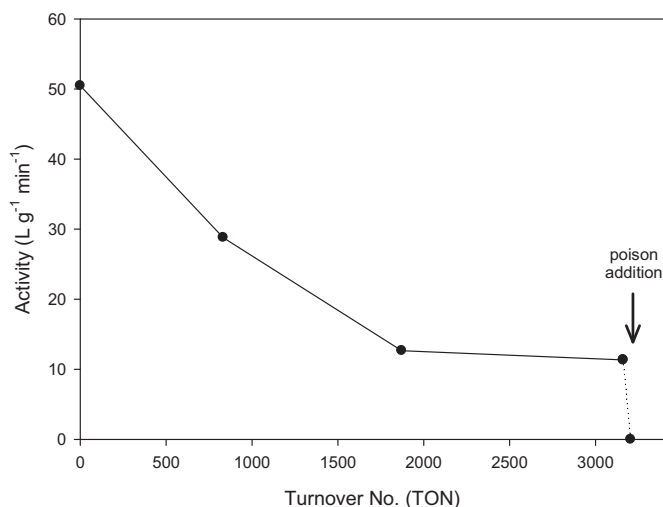

Fig. 4. The effect of the turnover number (TON) on the specific Pd activity for HDC ($C_{0,MCB}$ = 10 mg L^{-1}) in the wall-coated batch reactor (150 μm thick PDMS). The increase of the TON between the depicted activity measurements with MCB was achieved by batch-wise HDC of TCE. The catalyst poison Na$_2$SO$_3$ (1 mM) was added to the bulk solution before the last cycle (as indicated).

was estimated under the assumption that all pore volume is filled with HCl-saturated water (37%, w/w). However, only about 1/3 of the missing chloride could have dissolved in water-filled alumina pores. The formation of chlorinated silicone products could not be confirmed by GC–MS analysis, neither of the reactor headspace (e.g. methyl chloride) nor of silicone extracts (n-hexane). However, chlorinated silicone oligomers could be non-available for GC analysis. Although not proven, we tend to the opinion that the remaining chloride was mainly adsorbed to the alumina surface [33].

As also shown in Fig. 4, the catalyst, that had remained active over a wide TON range, was completely deactivated once sulphite was added to the reactor (last cycle). This implies that the polymer coating, which originally protected the catalyst against 1 mM sulphite, had been altered in such a way that it became more permeable for ionic compounds. A partial degradation of the PDMS under HDC reaction conditions was also indicated by GC–MS detection of various (non-chlorinated) hydrolysis products, such as methylated cyclosiloxanes [34]. Therefore, it is suggested that, due to HCl formed during the HDC reaction, gradual acid-induced degradation of the polymer occurred, so that eventually the polymer coating failed to provide protection to the catalyst.

3.3. Protection of pelletized catalyst

In the pelletized form (d_p = 3 mm), the non-coated Pd/Al$_2$O$_3$ catalyst exhibited a much lower apparent activity compared to the crushed material (d_p = 63–125 μm): A_{Pd} = 0.35 vs. 570 L g^{-1} min^{-1}, respectively. The difference amounts to about 3 orders of magnitude; it is mainly due to external (perforated PTFE cage, see Section 2) and internal (pore diffusion) mass-transfer resistances under batch conditions. Nevertheless, the pelletized form may be of some practical interest, because this is the preferred form of catalyst design in fixed-bed reactors for water treatment. Therefore, some attempts have been made to protect commercial 3 mm Pd/Al$_2$O$_3$ pellets against ionic catalyst poisons.

3.3.1. Silicone oil pore-filled pellets
Coating of Pd/Al$_2$O$_3$ particles with a polymer film may result in the accumulation of highly concentrated aqueous HCl inside the pores. In order to avoid this, a pore-filling approach was tested, in which the catalyst pores were filled with viscous silicone oil. Ideally, in an oil-filled porous catalyst, the metal clusters should be isolated from water so that the reaction takes place in an organic solvent environment. The question is: can HCl formed during the HDC reaction desorb from the surface and diffuse out to the bulk water phase, thereby minimizing the damage to the catalyst? Although the influence of the reaction media on the HDC reactions is not fully understood, several studies have reported slower reaction rates and/or faster deactivation of the catalyst when performed in organic solvents (e.g., THF and alcohols), compared to an aqueous system [35–38]. It was suspected that in the absence of water the desorption of HCl from the active sites could be hindered, resulting in lower catalyst activity and stability [35,37]. Alternatively, the influence of the solvent on reaction rates was attributed to the ability of the solvent to stabilize the reaction intermediates [36], to the solubility of the reactants in the solvent (and therefore the tendency to adsorb to or desorb from the catalyst) [39], or to the ability of the solvent to occupy and mask the catalytic sites [38]. Fritsch et al. [20] assume that surface-attached chloride is replaced by hydrogen molecules in PDMS-protected Pd systems. However, some catalyst deactivation was noted by the authors after several reaction runs.

In the present study, the HDC of MCB was measured in n-hexane and in THF (as aprotic water-repelling and water-miscible solvent, respectively), in order to evaluate the feasibility of the HDC in aprotic organic media and the effect of water on the reaction rates. These

Table 1
The effect of water content on the catalytic activity for hydrodechlorination of MCB in organic solvents. The catalyst was Pd/Al$_2$O$_3$, 63–125 μm size fraction.

Solvent	Water content (% v/v)	Catalyst	Catalytic activity A_{Pd} (L g^{-1} min^{-1})
Tetrahydrofuran	<0.005	Untreated catalyst	6.5
	2		8.7
	3.8		15
	5.7		22
	20		37
	100		570 ± 50[a]
n-Hexane	<0.01	Untreated catalyst	28
	<0.01	Dried catalyst	18

[a] Average value and one standard deviation from four measurements.

insights are necessary for an optimal design of oil- or polymer-modified catalysts. The obtained data are collected in Table 1. The HDC reaction takes place in all solvents at measurable rates. As expected, water has a positive effect on the HDC rates due to its ability to withdraw chloride from the Pd surface. However, even with a pre-dried catalyst in dry n-hexane, 3% of the maximum reaction rates in water were observed yet. It can be concluded that, although water is certainly the preferred reaction medium, HDC can also proceed at acceptable rates in non-polar organic media. This makes silicone coatings or fillings a promising reaction environment for Pd-catalysed HDC.

It is noteworthy that HDC is faster in n-hexane than in dry THF. Obviously, there is no simple correlation between reaction rates and solvent polarity. This is in contrast to findings of Keane et al. [36], who observed higher initial HDC rates for chlorobenzenes with increasing dielectric constants of solvent mixtures (THF–methanol–water). They link the observed solvent effects to the solvent's capacity to stabilize arenium intermediates at the catalyst surface. Non-polar solvents such as n-hexane or silicone oils were not included in this study. THF may form stronger surface complexes, which could hinder the pollutant attachment.

From the chemical point of view, silicone oil might be an effective protection medium for porous Pd catalysts. However, it was found that when pellets filled with silicone oil were shaken in water, the oil was slowly replaced by water and found as emulsion in the water phase, thus losing its protection function. A hydrophobization of the hydrophilic alumina surface by treatment with TMCS did not prevent the oil leaching. Therefore, we tried to seal the oil inside the pores by means of an additional external layer of rubbery PDMS (about 150 μm). The initial activity of the pore-filled catalyst with additional external rubbery PDMS layer was 0.34 L g^{-1} min^{-1}. The apparent activities of the unprotected and modified catalyst pellets were practically identical. This may be due to the fact that, for catalyst pellets, the apparent activity is dominated by mass-transfer effects rather than by inherent catalytic activities.

The HDC reaction with the pore-filled and coated pellets was measured both after pre-treatment with sulphite (100 mM, 3 d contact time) and in the presence of sulphite (1 mM). No oil emulsions were observed in the pre-treatment step; it caused no observable impact on the initial catalytic activity when the HDC was conducted afterwards in sulphite-free water (Fig. 5, filled symbols). This finding proves the feasibility in principle of the described catalyst design: the silicone filling and coating prevent any access of sulphite to the Pd sites. However, this protection was impaired when running the HDC cycles. After 8 reaction cycles in buffer solution with an approximately constant catalyst activity ($A_{Pd} \approx 0.3 \pm 0.1$ L g^{-1} min^{-1}), sulphite (1 mM, S: Pd$_{surface}$ = 27) was added to the catalyst suspension which caused rapid and complete deactivation (cycle no. 9 in Fig. 5). When sulphite (1 mM) was added from the beginning of a series of HDC experiments
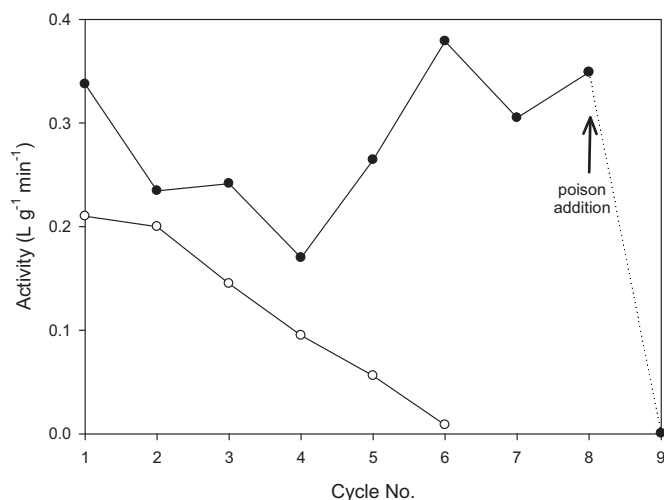

Fig. 5. Specific Pd activities for repeated HDC cycles of 10 mg L^{-1} MCB by a silicone-modified pelletized Pd/Al$_2$O$_3$ catalyst (silicone-filled pores + 150 μm PDMS coating). The bulk solution was either free of sulphite (filled symbols) or contained 1 mM of the catalyst poison Na$_2$SO$_3$ (open symbols). For the non-poisoned catalyst, Na$_2$SO$_3$ was added to the bulk solution before the last cycle (as indicated).

(open symbols in Fig. 5), the same silicone-modified catalyst lost its activity gradually. After the 5th reaction cycle (TON = 17), almost complete deactivation of the catalyst was observed. Since the catalytic activity remained relatively constant in the absence of sulphite, the observed deactivation is the result of sulphite rather than chloride poisoning. Both in presence and absence of sulphite, an increasing emulsification of the silicone oil was evident in the water phase which points to a gradual destruction of the polymer membrane or the silicone oil and an escape of the oil through defects in the PDMS membrane, possibly caused by acid-induced hydrolysis. Siloxane oligomers (hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, but no chlorinated Si products) were found, supporting the assumption of hydrolysis. It should be noted that, in contrast to silicone-film embedded catalysts (cf. Fig. 3), the recovery of chloride in the bulk water phase was complete, even from the first reaction cycle (data not shown). In other words, the transport of HCl through the oil-filled pores and the PDMS coating was not only possible but fast, while the penetration of sulphite towards the Pd sites seemed to be slow. This can possibly be attributed to the different solvation states of sulphite in water (ionic) and HCl in a silicone environment (non-ionic). This finding proves the basic idea of the described catalyst design: ionic catalyst poisons in the water phase are rejected from the polymer coating, while HCl can pass through this coating into the water phase. Unfortunately, we have not yet been successful in preparing long-term stable coatings with the specific polymer used.

Although emulsification of silicone oil in the water phase is a crucial phenomenon in the batch system, it is not clear how a silicone oil pore-filling behaves under fixed-bed conditions, where the extent of agitation is much lower than in a shaken catalyst suspension.

3.3.2. Double-layer rubbery two-component PDMS coating

In another approach for the protection of pelletized catalyst, the pellets were first impregnated with two-component PDMS dissolved in n-hexane and then coated with an additional outer PDMS layer. The amount of PDMS which penetrated into the alumina pores was smaller than with silicone oil, due to solvent evaporation which may cause holes. Presumably, the PDMS mostly formed an outer coating of the pellets. The initial activity of the pellets after this treatment was 1.1 ± 0.2 L g^{-1} min^{-1}, which was higher than for the non-coated pellets. This is probably either due to the omission
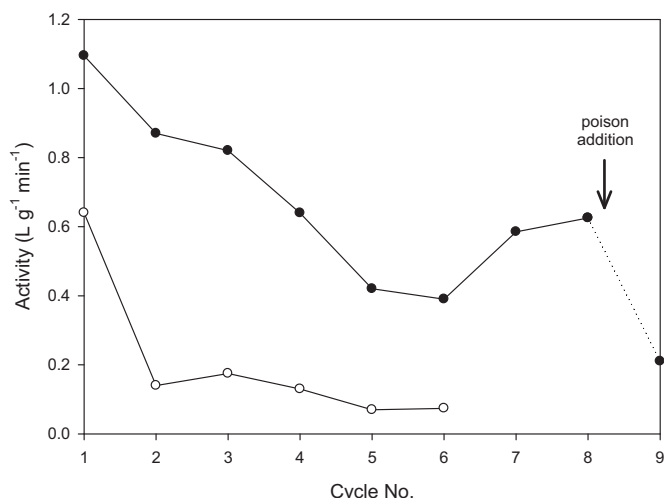
Fig. 6. Specific Pd activities for repeated HDC cycles of $10\,mg\,L^{-1}$ MCB by double-coated PDMS pellets. The bulk solution was either free of catalyst poison (filled symbols) or contained 10 mM of the catalyst poison Na_2SO_3 (open symbols). For the non-poisoned catalyst, Na_2SO_3 was added to the bulk solution before the last cycle (as indicated).

of the PTFE tube which was necessary for unprotected catalyst pellets (see experimental part) or an effect of pollutant sorption (and therefore concentration increase) near the reaction sites.

Results of a series of batch experiments with this catalyst are presented in Fig. 6. They are similar to those presented in Fig. 5: in the absence of sulphite, the catalyst is only gradually deactivated with increasing number of reaction cycles (filled symbols in Fig. 6). Addition of 10 mM sulphite after the 8th run caused a significant but not complete loss of the remaining activity. Chloride release from this catalyst was low at first, but increased gradually up to a final chloride recovery of 85% at the 8th cycle. When the catalyst was tested from the beginning in the presence of 10 mM sulphite (S: $Pd_{surface} = 270$), considerable deactivation of the catalyst was already observed in the first two cycles. The activity then levelled-off at about 15% of its initial level ($A_{Pd} \approx 0.1\,L\,g^{-1}\,min^{-1}$). Apparently, this catalyst coating succeeded in protecting some of the active Pd sites. No emulsification of the PDMS was observed during any of the reaction cycles. However, when comparing the two catalyst designs described in Figs. 5 and 6, it must be taken into account that the double-layer catalyst was tested under more severe conditions, i.e. 10 vs. 1 mM sulphite.

4. Conclusions

Several techniques for the protection of Pd/Al$_2$O$_3$ catalysts against catalyst poisons, using PDMS polymer coatings and pore-fillings, were tested. Sulphite was used as a model ionic compound. Our data suggest that the polymer coating can provide an initial high degree of protection for the catalyst, even at high sulphite concentrations up to 100 mM. However, this approach has been shown to be insufficient for protection under long-term reaction conditions, because the PDMS film gradually becomes permeable to ions, probably due to silicone hydrolysis initiated and promoted by the reaction product HCl.

There is still an eminent need to search for ways and means of protecting Pd-based catalysts from poisoning, because this problem prevents the wide application of Pd catalysts in water treatment processes. We suggest that for the purpose of protecting Pd catalysts from ionic poisons, as well as from self-poisoning by HCl, the catalyst should be embedded in or filled with an alternative reaction medium. This medium should be not only impermeable to ionic poisons, but also resistant towards the reaction product HCl, as well

as allowing HCl desorption and diffusion away from the catalyst surface. Batch experiments with dry organic solvents as reaction medium proved that Pd-catalysed HDC can proceed at reasonable rates in such an environment. The outstandingly high diffusivity of PDMS makes it a preferential candidate for polymer coatings, in order to minimize additional mass-transfer resistances. As yet, no optimal approach to overcoming the problems described above for Pd-based hydrodechlorination catalysts when using PDMS coatings is apparent.

Further studies on hydrogenation instead of hydrodechlorination with PDMS-modified Pd catalysts are planned. Hydrogenation as a model reaction allows testing of the long-term stability of polymer coatings beyond the limits imposed by the aggressive impact of HCl.

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